

Rapid eruption of silicic magmas from the Paraná magmatic province (Brazil) did not trigger the Valanginian event

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ABSTRACT

The Valanginian Stage is marked by a period of global positive $\delta^{13}\text{C}$ carbon cycle perturbation and biotic crises, which are collectively referred to as the Valanginian event (VE). Many attempts have been made to link the Paraná-Etendeka large igneous province volcanism with the VE. However, currently there is no conclusive proof to support this hypothesis, since the timing and duration of the volcanic activity are not known with sufficient precision. In this study, we significantly revise the time scales of magmatism and environmental impact of the Paraná magmatic province (PMP) in Brazil with new high-precision zircon U-Pb ages from the low-Ti Palmas and high-Ti Chapecó sequences. Our data demonstrate that significant volumes of low-Ti silicic rocks from the PMP erupted rapidly at ca. 133.6 Ma within 0.12 ± 0.11 k.y. The age of the high-Ti Chapecó sequence from central PMP is constrained at ca. 132.9 Ma and thus extends the duration of magmatic activity by ~700 k.y. Our new ages are systematically younger than previous ages and postdate the major positive carbon isotope excursion, indicating that PMP silicic magmatism did not trigger the VE but could have contributed to extending its duration. Within the framework of the stratigraphic column of the PMP, the earliest low-Ti basalts could have been responsible for the VE if they are at least 0.5 m.y. older than the low-Ti silicic rocks dated herein.

INTRODUCTION

Large igneous province (LIP) magmatism is thought to be responsible for global climate changes, some of which led to major mass extinction events during the Phanerozoic (e.g., Ernst and Youbi, 2017; Svensen et al., 2018). Isotopic proxies from the sedimentary record suggest that the effects of LIP emplacement include global warming and cooling, sea-level changes and shifts in seawater composition, and ocean acidification, stratification, or anoxia, resulting in black shale deposition (oceanic anoxic events [OAEs]; Percival et al., 2015). The Paraná-Etendeka LIP, with $\sim 1 \times 10^6$ km³ of preserved volcanic rocks of dominantly basaltic composition (Bellieni et al., 1986; Peate, 1997), is one of the world's largest LIPs, and it was emplaced coeval with the breakup of Gondwana and the opening of the South Atlantic Ocean dur-

ing the Early Cretaceous. Despite its size, the emplacement of the Paraná-Etendeka LIP had seemingly minor environmental effects (Charbonnier et al., 2017; Svensen et al., 2018). The current paradigm suggests a temporal correlation between the Paraná-Etendeka LIP and the Valanginian event (VE), which was an episode of environmental change characterized by global-scale carbon cycle perturbation and a biotic crisis, recorded by a positive $\delta^{13}\text{C}$ shift and Hg enrichment in the sedimentary record (e.g., Erba et al., 2004; Martinez et al., 2015; Charbonnier et al., 2017).

The onset of the VE was previously estimated at 136.8 ± 1.3 Ma (Sprovieri et al., 2006), but it has recently been revised to 135.22 ± 1.00 Ma based on integrated geochronology and astrochronology (Martinez et al., 2015).

However, to prove a temporal connection between the Paraná volcanism and the VE, we must have knowledge of the precise timing and

duration of the volcanic activity. In this contribution, we significantly revise the time scales of magmatism and environmental impact of the Paraná magmatic province (PMP) in Brazil, the South American part of the Paraná-Etendeka LIP, via high-precision zircon U-Pb chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) dating.

GEOLOGY, GEOCHRONOLOGY, AND SAMPLE MATERIAL

Silicic volcanic rocks from the PMP (Fig. 1) are relatively abundant compared to other continental flood basalt provinces (e.g., Deccan Traps, Central Atlantic magmatic province). In Brazil, the $\sim 15,000$ km³ of preserved silicic rocks are divided into low-Ti (Palmas) and high-Ti (Chapecó) lithologies (Bellieni et al., 1986; Garland et al., 1995; Peate, 1997; Nardy et al., 2008). The largest volume of low-Ti Palmas-type rocks is concentrated in the south of the PMP and comprises the chemically distinct Anita Garibaldi, Jacuí, and Caxias do Sul dacites (Nardy et al., 2008), which cover or are interbedded with the first low-Ti basaltic flows (Gramado type; Fig. 1). At the top of the sequence, above the dacites and the low-Ti basalts, there is the Santa Maria rhyolite. The silicic high-Ti Chapecó rocks comprise several trachydacites (Guarapuava, Tamarana, and Ourinhos types) and cover the low-Ti basaltic and silicic rock sequence to the center and north of the PMP (Peate, 1997; Nardy et al., 2008; Janasi et al., 2011).

Previous estimates of the timing and duration of the volcanism in the southern PMP were based on ⁴⁰Ar–³⁹Ar and U–Pb secondary ion mass spectrometry (SIMS) data and cluster at 135–134 Ma (Fig. 2A; Renne et al., 1992; Thiede and Vasconcelos, 2010; Pinto et al.,

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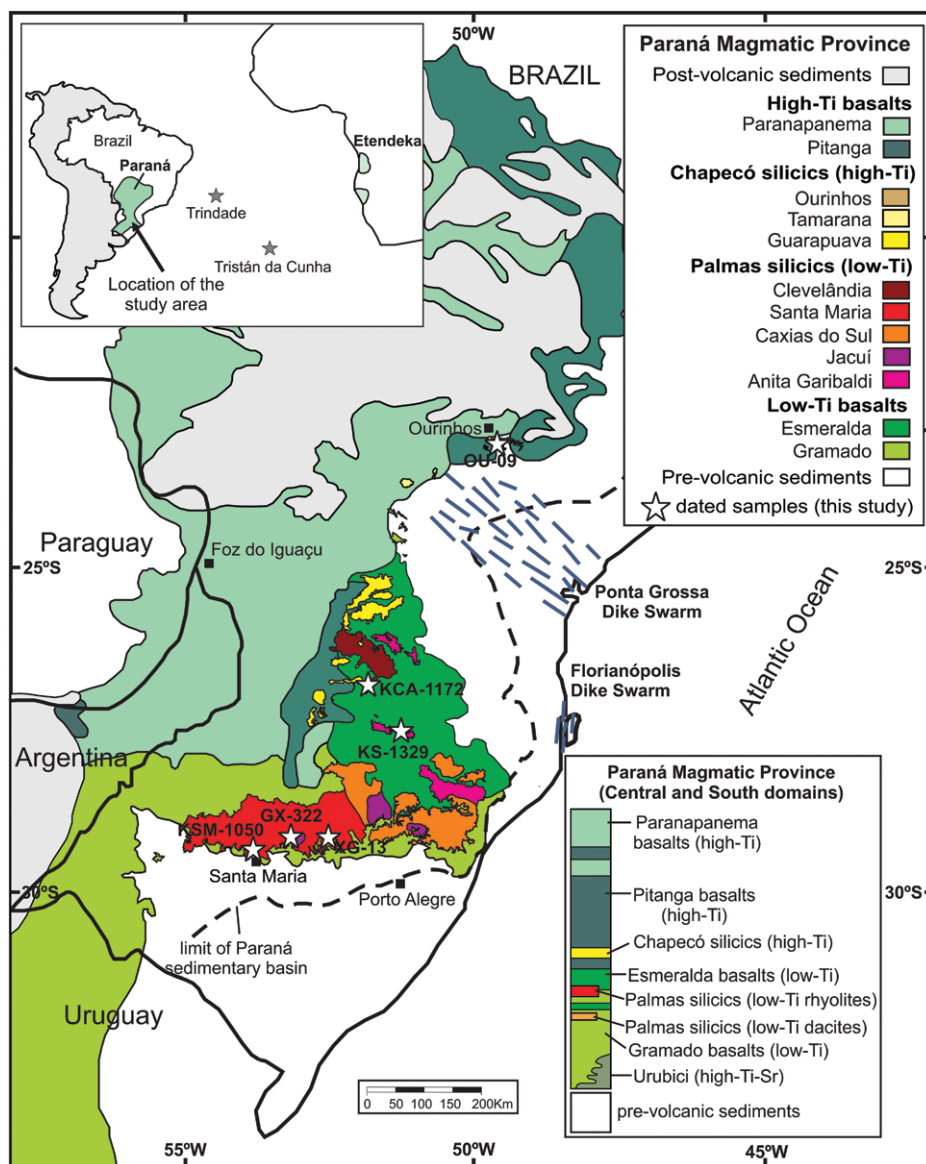


Figure 1. Geological map of the Paraná magmatic province (PMP) in Brazil showing location of samples selected for dating (modified from Janasi et al., 2011; Lucchetti et al., 2018). Inset shows position of PMP and correlated rocks in Etendeka, Africa.

2011; Baksi, 2018). Zircon and baddeleyite ID-TIMS U-Pb ages reported for the Ourinhos trachydacite (Janasi et al., 2011) and for the Florianópolis and Ponta Grossa dike swarms (Florisbal et al., 2014; Almeida et al., 2018) range between 134.7 and 133.4 Ma (Fig. 2A). Published ages from the PMP are illustrated in Figure 2A along with the U-Pb data set from this study, demonstrating that the ^{40}Ar - ^{39}Ar and SIMS U-Pb data have higher uncertainties and more scatter.

Here, we dated zircon from six silicic volcanic rocks from the two major geochemically distinct sequences of the PMP (Fig. 1): (1) low-Ti Palmas sequence: Santa Maria rhyolite (KSM-1050) and Anita Garibaldi (KS-1329), Jacuí (GX-322), and Caxias do Sul (XG-13) dacites; and (2) high-Ti Chapecó sequence: Guarapuava trachydacite (KCA-1172) and the Ourinhos tra-

chydacite sample (OU-09) previously dated in Janasi et al. (2011) at 134.3 ± 0.8 Ma.

METHODS

High-precision TIMS U-Pb zircon ages were obtained at the University of Geneva by CA-ID-TIMS and corrected for initial ^{230}Th disequilibrium. All reported weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages are given with $[X]/[Y]/[Z]$ uncertainties (Schoene et al., 2006) at the 2σ level. Full details on sample preparation and methodology are provided in the Supplemental Material¹. Hafnium isotopic compositions were measured on

¹Supplemental Material. Sample description, sample preparation, analytical protocols, zircon U-Pb and Hf data, and additional interpretations on zircon ages. Please visit <https://doi.org/10.1130/10.1130/GEOL.S.12678926> to access the supplemental material, and contact editing@geosociety.org with any questions.

a Neptune multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) at the University of Geneva. The analytical techniques and the data reduction followed those outlined in Farina et al. (2018).

RESULTS

In total, 40 concordant U-Pb single-grain zircon ages were obtained along with Hf isotopic compositions of several dated crystals (Fig. 2B). The latter were used to evaluate the melt sources and to assist in the interpretation of dates (Schaltegger and Davies, 2017). Most of the analyzed zircon grains provided Cretaceous crystallization ages (Fig. 3), but a few inherited grains with ages of 1.1–0.6 Ga were also identified in three of the four low-Ti silicic samples. Detailed information on the dated samples, analytical techniques, and data sets is provided in the Supplemental Material.

The 13 analyzed zircon crystals from the Anita Garibaldi dacite (KS-1329) displayed an age spread of ~70,000 k.y. A weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $133.536 \pm 0.049/0.076/0.16$ Ma (mean square of weighted deviates [MSWD] = 1.4; $n = 7$) from the seven youngest concordant grains is the best estimate for the eruption age, assuming the optimal chemical-abrasion conditions were enough to remove the effects of Pb loss. All five concordant zircon grains from the Jacuí dacite (GX-322) yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $133.575 \pm 0.078/0.099/0.17$ Ma (MSWD = 2; $n = 5$). Six zircons were analyzed from the Caxias do Sul dacite (XG-13), including one Neoproterozoic xenocryst, and a grain with an age of ca. 127 Ma that was interpreted to result from Pb loss. The four remaining zircon grains yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $133.638 \pm 0.071/0.092/0.17$ Ma (MSWD = 1.3; $n = 4$). The tiny, U-rich zircon crystals from the Santa Maria rhyolite (KSM-1050) were chemically abraded at 180 °C for only 30 min to prevent total dissolution. Two grains were discarded, a Paleoproterozoic xenocryst and a grain at ca. 128 Ma. The remaining five grains yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $133.66 \pm 0.10/0.12/0.19$ Ma (MSWD = 2.1; $n = 5$).

Two zircon grains were extracted from the Guarapuava trachydacite (KCA-1172), yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $132.906 \pm 0.072/0.092/0.17$ Ma (MSWD = 1). Three grains from the Ourinhos trachydacite (OU-09) contained very low abundances of radiogenic Pb (down to 37 fg), but due to the low Pb blanks at the University of Geneva, this sample yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of $132.72 \pm 0.76/0.77/0.78$ Ma (MSWD = 0.71).

In summary, the low-Ti Palmas dacites and rhyolites erupted at 133.6 ± 0.11 Ma within a narrow time interval of 0.12 ± 0.11 k.y., and the high-Ti Chapecó trachydacites erupted at 132.9 Ma within ~0.76 k.y.

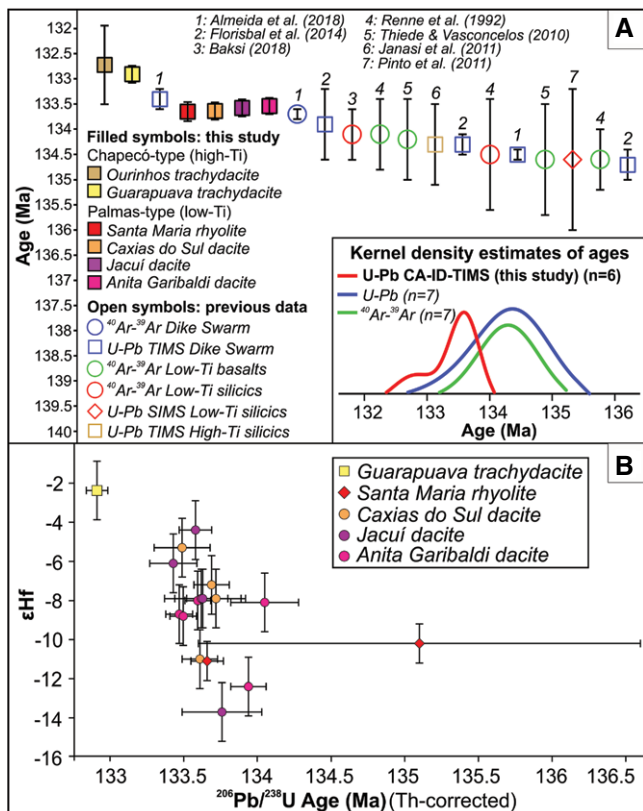


Figure 2. (A) Summary of geochronology data from the Paraná magmatic province (PMP, Brazil), comparing zircon U-Pb chemical-abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) ages from this study (filled squares; [Z] uncertainties included) with previously published data (open circles, squares, and diamond; [X] uncertainties included). Kernel density estimates of ages are shown in the lower right. Compared to other studies, zircon was chemically abraded (CA) and mixed with EARTH-TIME ET535 isotope tracer solution (<http://www.earthtimetests.com/working-groups/u-pb-isotope-dilution/et535-and-et2535/>; Condon et al., 2015), enabling more precise and accurate age estimates. SIMS—secondary ion mass spectrometry. (B) Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages and corresponding $\epsilon_{\text{Hf}}(t)$ values for PMP silicic volcanic rocks.

DISCUSSION

Timing and Duration of Silicic Magmatism in the Paraná Magmatic Province

Our new high-precision U-Pb ages demonstrate that significant volumes of silicic magma from the PMP erupted very rapidly

(Fig. 3). When the decay constant uncertainties are included, the weighted mean ages of the low-Ti Palmas sequence overlap with the average $^{40}\text{Ar}/^{39}\text{Ar}$ age (flux-monitor corrected to the 28.201 Ma Fish Canyon sanidine age of Kuiper et al., 2008) of 133.7 ± 0.2 Ma of the cor-

related low-Ti silicic sequence from Etendeka in Africa (Renne et al., 1996). However, our new ages (Fig. 2A) are systematically younger than (although there is some overlap) the $^{40}\text{Ar}/^{39}\text{Ar}$ age estimates from the south PMP presented by Renne et al. (1992), Thiede and Vasconcelos (2010), and Baksi (2018), which came mostly from basaltic sequences but also included some silicic rocks from the sequences dated here.

The high-Ti Chapecó sequence yielded slightly younger ca. 132.9 Ma ages, favoring northern migration of volcanism (Peate et al., 1990; Ernesto et al., 1999; Janasi et al., 2011), which is also in agreement with ca. 133.6–131.5 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ ages from high-Ti basalt sills (Ernesto et al., 1999). The Ourinhos dacite sample previously dated by U-Pb TIMS by Janasi et al. (2011) at 134.3 ± 0.8 Ma was reanalyzed here, and the new result (132.72 ± 0.76 Ma; OU-09) is identical to our age for the other Chapecó-type trachydacite (132.906 ± 0.072 Ma; KCA-1172). Therefore, our new data fit the stratigraphy better and reveal that the high-Ti silicic volcanism was ~1.5 m.y. younger than previously estimated.

Evaluating a Possible Link between Paraná Magmatic Province Volcanism and the Valanginian Environmental Crisis

The low-Ti silicic volcanism dated here belongs to the stratigraphically oldest part of the PMP lavas in Brazil and is at least 0.5 m.y. younger than the youngest 135.22 ± 1.0 Ma astronomical age for the onset of the VE (Martinez et al., 2015) and indicative of a short magmatic episode of ca. 100 k.y. The VE is defined by a 1.5‰–2‰ and up to 4‰–5‰ positive $\delta^{13}\text{C}$

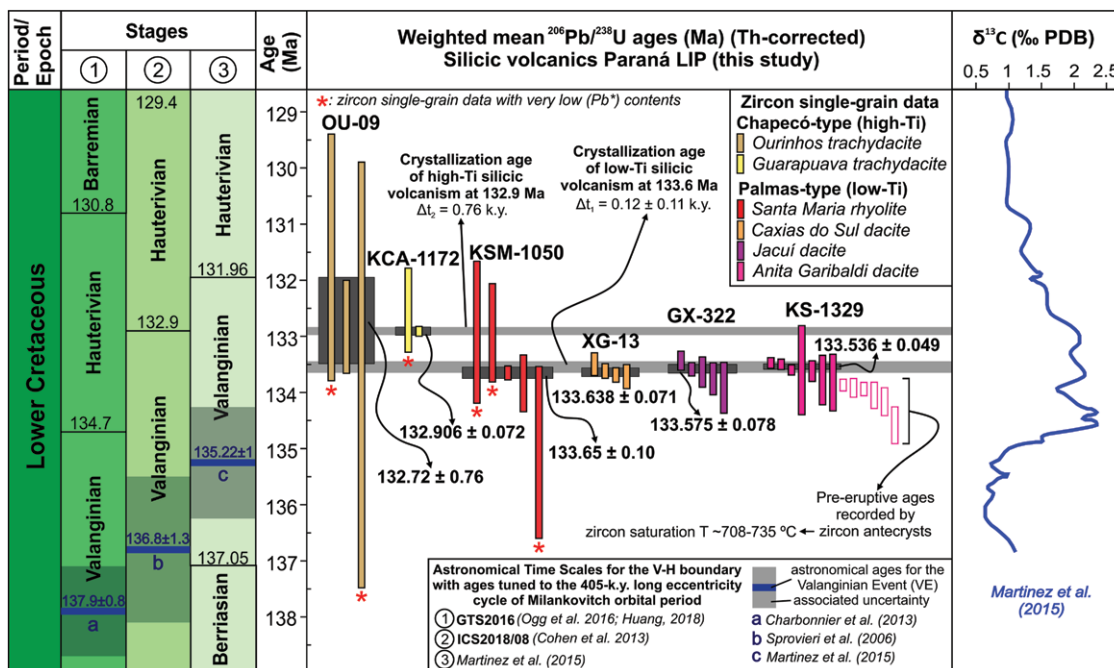


Figure 3. Left: Various suggested time scales for the Valanginian-Hauterivian (V-H) boundary and astronomical ages for the Valanginian event (VE; horizontal blue lines and gray bars). Middle: Rank-order plot of U-Pb chemical-abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) data from the Paraná large igneous province (LIP, Brazil) silicic volcanic rocks, where colored vertical bars are single-zircon ages including 2σ uncertainties. Filled bars were used in weighted mean age calculations (horizontal dark-gray bars). Red asterisks are zircon single-grain data with very low radiogenic Pb content (Pb^*). Right: Carbon isotope excursion ($\delta^{13}\text{C}$) associated with the VE according to Martinez et al. (2015).

anomaly in the marine and terrestrial records, respectively (e.g., Erba et al., 2004; Gröcke et al., 2005), and this has been used to infer a protracted period of global cooling, together with Hg enrichment in marine sediments (Charbonnier et al., 2017).

The Paraná-Etendeka LIP has been suggested as the cause of the VE, but our new U-Pb data indicate that the silicic magmatism postdated the major positive carbon shift (Fig. 3). Therefore, the PMP silicic volcanism is unlikely to have been the triggering mechanism responsible for the onset of the environmental changes during the VE (Fig. 3). However, the $\delta^{13}\text{C}$ record reaches a postexcursion value that remains relatively stable thereafter, and the Paraná silicic LIP volcanism could have contributed to sustaining the VE. This conclusion is only strictly valid for the silicic volcanism dated in this study. We speculate that pre-silicic low-Ti basalts could have been responsible for the VE if they are at least 0.5 m.y. older than the silicic rocks dated here. These belong to the Gramado-type and the geographically more restricted Urubici-type basalts. Dikes interpreted as feeders of the Urubici basalts were dated by U-Pb TIMS at 134.7 ± 0.3 – 133.9 ± 0.7 Ma (Florisbal et al., 2014), and low-Ti Gramado basalts were dated with $^{40}\text{Ar}/^{39}\text{Ar}$ to 134.1 ± 0.7 Ma (Renne et al., 1992), attesting to this possibility. However, as the ages of the Urubici and Gramado dikes and basalts also overlap within error with our new U-Pb ages, their association with the VE remains uncertain until more precise age estimates are obtained.

The temporal correlation between the PMP volcanism and the VE also relies on the assumption that the geological time scale (GTS) is correct. There are some discrepancies in the present definition of stage boundaries. Different astronomical time scales for the Valanginian-Hauterivian boundary are illustrated in Figure 3, with ages tuned to the 405-k.y.-long eccentricity cycle along with proposed astronomical ages and associated uncertainties for the VE. The GST2016 (Ogg et al., 2016) and recent compilation by Huang (2018) report the 137.9 ± 0.8 Ma age from Charbonnier et al. (2013) for the VE, and they use a 4.695 m.y. duration for the Valanginian Stage. The 136.8 ± 1.3 Ma age for the VE proposed by Sprovieri et al. (2006) was published in the *ICS International Chronostratigraphic Chart* 2018/08 (Cohen et al., 2013), along with a longer duration of 6.9 m.y. for the Valanginian Stage. Even the youngest age reported for the VE of 135.22 Ma (Martinez et al., 2015) is older and does not overlap with our new U-Pb data. This further reinforces our inference that the PMP silicic eruptions were not the cause of the VE, implying that they also could not have been responsible for the Pb isotope signature of Ocean Drilling Program (ODP) Site 1149B sediments from the interval of the VE positive $\delta^{13}\text{C}$ excursion, as suggested by Peate (2009).

The question remains as to why the rapid emplacement of extremely large volumes of magmatic material during the main stages of the PMP did not trigger a severe global-scale mass extinction. Several hypotheses have been suggested for how LIP events can cause large environmental perturbations, including magma degassing or the release of toxic volatiles from sediments, either through assimilation or contact metamorphism (e.g., Ganino and Arndt, 2009). High-precision U-Pb geochronology has provided evidence for the latter by correlating magmatic intrusions into volatile-rich sedimentary basins of the Central Atlantic magmatic province (Davies et al., 2017) and the Siberian Traps (Svensen et al., 2009) with major environmental and biotic crises. Sills are abundant in the PMP, where they may reach an integrated thickness up to 1 km in places, but the volume of organic-rich shales and dolomitic limestones (i.e., Irati Formation) may be too limited to have released large volumes of volatiles. Although, on the basis of chemical affinities, it is usually assumed that sills and extrusive products in the PMP are largely coeval, further high-precision geochronological work is required to confirm this hypothesis.

CONCLUSIONS

All varieties of the Palmas-type silicic volcanic rocks in the southern part of the Paraná magmatic province erupted very rapidly within an extremely narrow time interval of 0.12 ± 0.11 k.y. and have indistinguishable zircon U-Pb ages of ca. 133.6 Ma, which are ~ 0.5 m.y. younger than the youngest age estimate for the onset of the VE and its associated $\delta^{13}\text{C}$ excursion, biotic changes, and the positive Hg anomaly in the sedimentary record. Zircon U-Pb ages of ca. 132.9 Ma for the Chapecó sequence in the central part of the PMP are ~ 1.5 m.y. younger than previously estimated. Our new high-precision estimates for the eruptive age of the PMP imply a northward migration of the volcanism, which is in agreement with stratigraphy, and these results indicate that the duration of silicic magmatism is ~ 700 k.y. Thus, the short-lived low-Ti silicic volcanism of the PMP was not the trigger of the VE, although it could have contributed to its extension, considering a duration of 6 m.y. for the VE. Further geochronological work focused on the older low-Ti basalt units and on the PMP intrusive magmatism is needed to fully evaluate the connection between the province and potential environmental effects.

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